



⑪ ① CA No. 893191

④ ISSUED Feb. 15, 1972

⑤ CLASS 402-267
C.R. CL. 402-265

NATIONAL REFERENCE LIBRARY
OF SCIENCE AND INVENTION

3 MAR 1972

⑩ **CANADIAN PATENT**

⑤④ **PROCESS FOR REACTING A PHENOL WITH A VICINAL
EPOXY COMPOUND**

William O. Perry, Lake Jackson, Texas, U.S.A.

Granted to The Dow Chemical Company, Midland, Michigan,
U.S.A.

②① APPLICATION No. 089, 148
②② FILED July 24, 1970

③① PRIORITY DATE May 28, 1970 (14, 618) U.S.A.

No. OF CLAIMS 18 - No drawing

This publication is a photographic reproduction of the specification filed by the applicant for patent of invention. Any spelling or grammatical errors in the specification are the responsibility of the patentee.

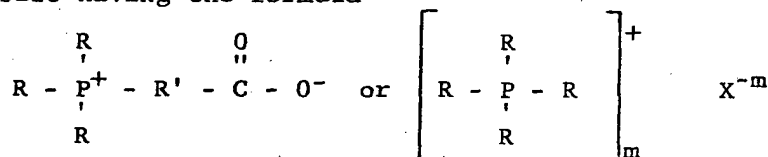
Cette publication est une reproduction photographique du mémoire descriptif déposé par le demandeur d'un brevet d'invention. Le breveté assume la responsabilité de toute erreur orthographique ou grammaticale dans le mémoire descriptif.

893191

This invention concerns a process for the preparation of hydroxy ethers whereby an aromatic hydroxyl-containing compound is reacted with a 1,2-epoxy-containing compound in the presence of a catalyst. The invention also concerns polyepoxide compositions.

It is well known in the art to produce hydroxyl-containing ethers by reacting a vicinal epoxy-containing compound with a phenolic hydroxyl-containing compound in the presence of such catalysts as tertiary amines, quaternary ammonium halides, and phosphonium halides and the like.

The present invention provides a process for preparing a hydroxy ether by reacting an aromatic hydroxy-containing compound with a 1,2-epoxy-containing compound in presence of a catalyst characterized in that the catalyst employed is a phosphonium salt having the formula



wherein each R is hydrogen, an aliphatic hydrocarbon radical containing from 1 to 20 carbon atoms, an aromatic hydrocarbon radical, an alkyl substituted aromatic hydrocarbon radical, or -R''Y wherein R'' is an aliphatic hydrocarbon radical having from 1 to 20 carbon atoms and Y is Cl, Br, I, NO₂, or OH; R' is an alkylene group having from 2 to 20 carbon atoms; X is the anion portion of an acid or acid ester selected from carboxylic, polycarboxylic, carbonic, phosphoric, phosphonic, phosphinic, nitric, nitrous, sulfuric, sulfinic, sulfonic, silicic, and boric acids; and m is the valence of the anion X.

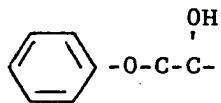
This invention also relates to compositions comprising a polyepoxide and a phosphonium salt as defined above.



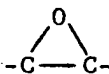
893191

The process of the present invention not only provides a novel catalyst system for promoting the reaction between a phenolic hydroxyl-containing compound and an epoxy-containing compound, but provides certain valuable improvements in the products produced by employing such catalyst systems. Among the improvements provided by this invention are less color in the product, and in the instance of those catalysts containing no halogen substituents, improved electrical properties can be achieved in the cured products. An additional and important advantage of the present process is observed when reacting a dihydric phenol such as a bisphenol or a dihydroxy benzene with a diepoxide to produce high molecular weight resins in that products obtained when the catalysts of the present invention are employed are much higher in molecular weight than the products produced when the phosphonium halide catalysts of the known art are employed.

The process of the invention involves the reaction of any epoxy compounds and any phenol to form a hydroxy ether



The epoxy compounds used are those possessing at least one 1,2-epoxide group, i.e., a group having the formula



They may be monoepoxides or polyepoxides. The monoepoxides may be aliphatic or cycloaliphatic or heterocyclic and may be saturated or unsaturated. They may also be substituted with aromatic rings, ether groups, halogen atoms, ester groups, and the like. Examples of the monoepoxides include, among others, styrene oxide, phenyl glycidyl ether, allyl glycidyl ether, octadecyl glycidyl ether,

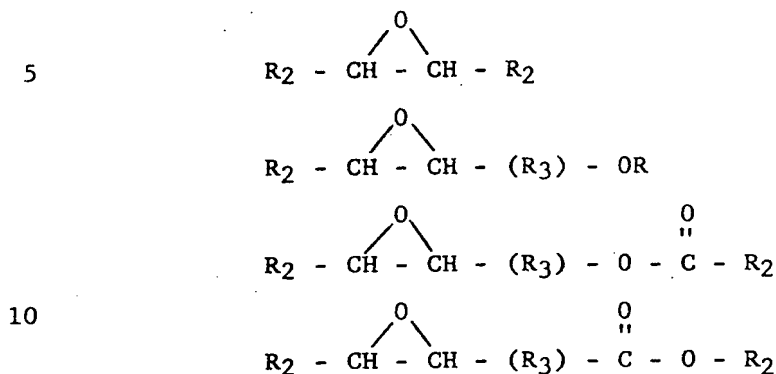
amyl glycidyl ether, tolyl glycidyl ether, chlorophenyl glycidyl ether, naphthyl glycidyl ether, diacetate of monoglycidyl ether of glycerol, dipropionate of the monoglycidyl ether of glycerol, diacrylate of the monoglycidyl ether of glycerol, 1,2-hexylene
5 oxide, ethylene oxide, propylene oxide, 1-heptylene oxide, 3-ethyl-1,2-pentylene oxide, glycidyl acetate, glycidyl benzoate, glycidyl propionate, glycidyl acrylate, glycidyl allyl phthalate, glycidyl methyl maleate, glycidyl stearate, glycidyl oleate, methyl 1,2-epoxypropionate, butyl 1,2-epoxypropionate, and the like.

10 Preferred monoepoxides to be used include the mono-epoxy-substituted hydrocarbons, such as, for example, the alkylene oxides containing up to 12 carbon atoms, the epoxy-substituted hydrocarbons, such as, for example, epoxy cyclohexane, or epoxy-propylbenzene; the monoepoxy substituted alkyl ethers of hydro-
15 carbon monohydric alcohols or phenols, such as, for example, the glycidyl ethers of aliphatic, cycloaliphatic or aromatic hydrocarbon alcohols containing up to 12 carbon atoms; the mono-epoxy-substituted alkyl esters of hydrocarbon monocarboxylic acids, such as, for example, the glycidyl esters of aliphatic, cycloaliphatic
20 or aromatic hydrocarbon acids, as glycidyl acrylate, glycidyl caprolate, and glycidyl benzoate; the monoepoxy-substituted alkyl esters of hydrocarbon polycarboxylic acids wherein the other carboxyl group or groups are esterified with alkanols, such as, for example, glycidyl esters of phthalic acid, maleic acid, iso-
25 phthalic acid, or succinic acid; wherein each contains up to 15 carbon atoms; alkyl and alkenyl esters of epoxy-substituted monocarboxylic acids, such as esters of 1,2-epoxy-propionic acid, epoxy butyric acid or epoxy pentanoic acid; and epoxyalkyl ethers of polyhydric alcohols wherein the other OH groups are esterified
30 or etherified with hydrocarbon acids or alcohols, such as, for example, monoglycidyl ethers of aliphatic, cycloaliphatic polyhydric

893191

alcohols, or polyhydric phenols, each containing no more than 15 carbon atoms.

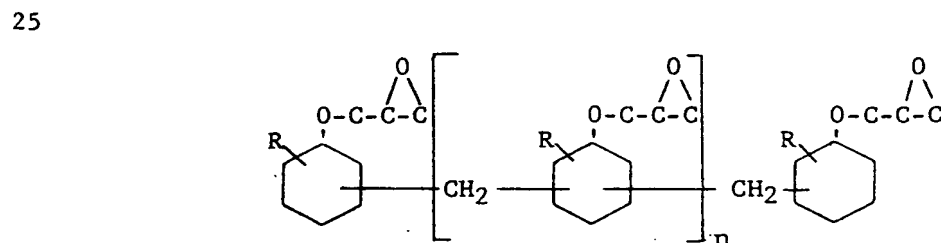
Other monoepoxides are those of the formula



wherein R_2 is hydrogen, a hydrocarbon or halogenated hydrocarbon radical and R_3 is a bivalent hydrocarbon or halogenated bivalent hydrocarbon radical, preferably containing 1 to 12 carbon atoms.

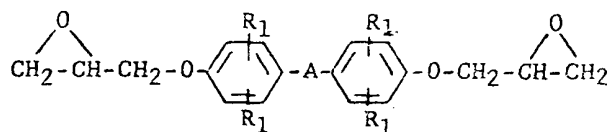
The polyepoxides used in the process of the invention may be saturated or unsaturated, aliphatic, cycloaliphatic, aromatic, or heterocyclic and may be substituted if desired with non-interfering substituents, such as halogen atoms, phosphorus atoms, hydroxyl groups, or ether radicals. They may also be monomeric or polymeric.

Examples include the glycidyl ethers of novolac resins, i.e., phenol-aldehyde condensates. Preferred resins of this type are those of the formula:

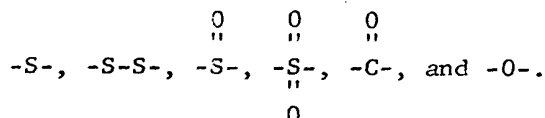


wherein R is hydrogen or an alkyl radical and n is an integer of 1 to about 10.

The preferred polyepoxides are those represented by the general formula:



wherein each R_1 is hydrogen, bromine, or chlorine and wherein A is an alkylene or alkylidene group having from 1 to 4 carbon atoms,



Other examples include the epoxidized esters of the polyethylenically unsaturated monocarboxylic acids, such as epoxidized linseed, soybean, perilla, oiticica, tung, walnut or dehydrated castor oil, methyl linoleate, butyl linoleate, ethyl 9,12-octadecandienoate, butyl 9,12,15-octadecatrienoate, butyl oleostearate, mono or diglycerides of tung oil, fatty acids, monoglycerides of soybean oil, sunflower, rapeseed, hempseed, sardine, or cottonseed oil.

Another group of the epoxy-containing materials that may be used in the process of the invention includes the epoxidized esters of unsaturated monohydric alcohols and polycarboxylic acids, such as, for example, diglycidyl phthalate, diglycidyl adipate, diglycidyl isophthalate, di(2,3-epoxybutyl) adipate, di(2,3-epoxybutyl) oxalate, di(2,3-epoxyhexyl) succinate, di(3,4-epoxybutyl) maleate, di(2,3-epoxyoctyl) pimelate, di(2,3-epoxybutyl) phthalate, di(2,3-epoxyoctyl) tetrahydrophthalate, di(4,5-epoxydodecyl) maleate, di(2,3-epoxybutyl) terephthalate, di(2,3-epoxypentyl) thiodipropionate, di(5,6-epoxytetradecyl) diphenyl-

dicarboxylate, di(3,4-epoxyheptyl) sulfonylidibutyrate, tri(2,3-epoxybutyl) 1,2,4-butanetricarboxylate, di(5,6-epoxypentadecyl) tartarate, di(4,5-epoxytetradecyl) maleate, di(2,3-epoxybutyl) azelate, di(3,4-epoxybutyl) citrate, di(5,6-epoxyoctyl) cyclo-
 5 hexane-1,3-dicarboxylate, di(4,5-epoxyoctadecyl) malonate.

Another group of the epoxy-containing materials includes those epoxidized esters of unsaturated alcohols and unsaturated carboxylic acids, such as glycidyl glycidate; 2,3-epoxybutyl 3,4-epoxypentanoate; or 3,4-epoxyhexyl 3,4-epoxypentanoate.

10 Still another group of the epoxy-containing materials includes epoxidized derivatives of polyethylenically unsaturated polycarboxylic acids, such as, for example, dimethyl 8,9,12,13-diepoxyeicosanedioate; dibutyl 7,8,11,12-diepoxyoctadecanedioate; dioctyl 10,11-diethyl-8,9,12,13-diepoxyeicosanedioate; dihexyl
 15 6,7,10,11-diepoxyhexadecanedioate; didecyl 9-epoxyethyl-10,11-epoxyoctadecanedioate; dibutyl 3-butyl-3,4,5,6-diepoxycyclohexane-1,2-dicarboxylate; dicyclohexyl 3,4,5,6-diepoxycyclohexane-1,2-dicarboxylate; dibenzyl 1,2,4,5-diepoxycyclohexane-1,2-dicarboxylate; or diethyl 5,6,10,11-diepoxyoctadecyl succinate.

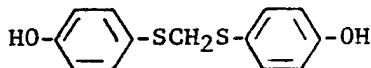
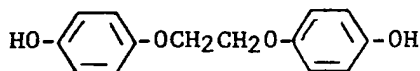
20 Still another group comprises the epoxidized polyethylenically unsaturated hydrocarbons, such as epoxidized 2,2-bis(2-cyclohexenyl)propane, epoxidized vinyl cyclohexene or epoxidized dimer of cyclopentadiene.

The phenols used in the process of the invention are
 25 those compounds possessing at least one OH group attached to an aromatic nucleus. The phenols may be monohydric or polyhydric and may be substituted with a great variety of different types of substituents. Examples of the phenols include among others, phenol, resorcinol, o-cresol, m-cresol, p-cresol, carvacrol,
 30 thymol, chlorophenol, nitrophenol, dinitrophenol, picric acid, pyrocatechol, hydroquinone, pyrogallol, hydroxyhydroquinone,

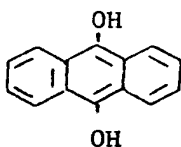
893191

phloroglucinol, 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis(4-hydroxyphenyl)pentane, 2,2-bis(4-hydroxyphenyl)phloroglucinol, bis(4-hydroxyphenyl)methane, 2-methoxyphenol, 2,4-dibutoxyphenol, 2,5-dichlorophenol, 3-acetoxyphenol, 2,2-bis(3-allyl-4-hydroxy-
 5 phenyl)propane, 2,2-bis(3-isobutyl-4-hydroxyphenyl)pentane, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, 1,1,4,4-tetrakis(4-hydroxyphenyl)-pentane, and polymeric type polyhydric phenols obtained by condensing monohydric or polyhydric phenols with formaldehyde, as well as phenols of the formulae

10



15

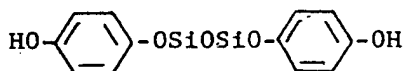
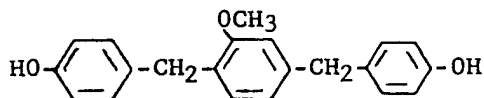


20

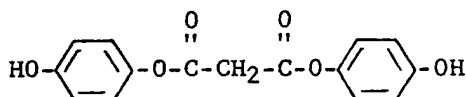


n is to 25

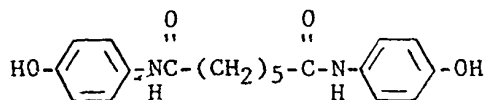
25



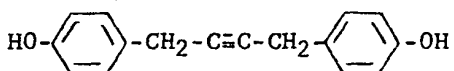
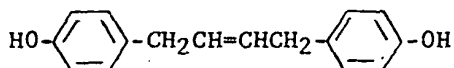
30



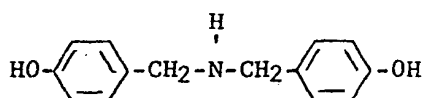
893191



5

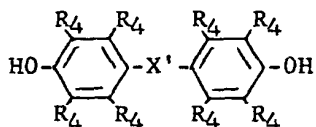


10



Preferred phenols to be used are the polyhydric phenols containing from 2 to 6 OH groups and up to 30 carbon atoms. Coming under special consideration are the phenols of the formula

15

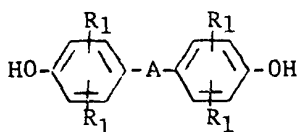


wherein X' is a polyvalent element or radical and each R₄ is a member of the group consisting of hydrogen, halogen and hydrocarbon radicals. The preferred elements or radicals represented by X' are oxygen, sulfur, -SO-, -SO₂-, bivalent hydrocarbon radicals containing up to 10 carbon atoms, and oxygen, sulfur and nitrogen-containing hydrocarbon radicals, such as -OR₅O-, -OR₅OR₅O-, -S-R₅-S-, -S-R₅-S-R₅-S-, -OSiO-, -OSiOSiO-,

$$\begin{array}{ccccccc} \text{O} & \text{O} & \text{O} & \text{O} & \text{O} & \text{O} \\ \parallel & \parallel & \parallel & \parallel & \parallel & \parallel \\ -\text{O}-\text{C}-\text{O}- & -\text{C}-\text{O}-\text{R}_5-\text{O}-\text{C}- & -\text{S}-\text{R}_5-\text{S}- & -\text{SO}_2-\text{R}_5-\text{SO}_2- \end{array}$$
 radicals wherein R₅ is a bivalent hydrocarbon radical.

Having regard to availability and economy it is most preferred that the aromatic hydroxy-containing compound is a bisphenol having the formula

893191



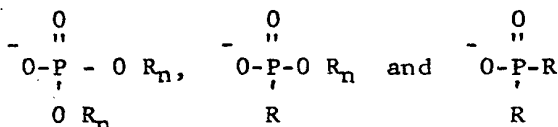
5 wherein each R_1 is hydrogen, chlorine, or bromine, and A is an alkylene or alkylidene group having from 1 to 4 carbon atoms, -S-, -S-S-, -SO-, -SO₂-, -CO-, or -O-.

One group of catalysts employed in this invention are the phosphonium salts wherein the anion X is



Suitable such phosphonium salts of a nitrogen-containing acid include, for example, ethyltriphenylphosphonium nitrate, and ethyltriphenylphosphonium nitrite.

15 Another group of catalysts employed in the present invention are the phosphonium salts wherein the anion X is

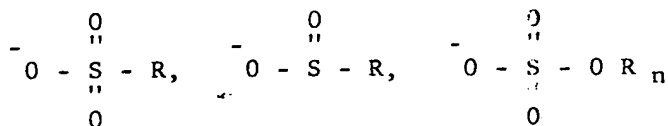


20 wherein each R is as defined hereinbefore and wherein each n is zero or 1.

Suitable such phosphonium salts include, for example, ethyltriphenylphosphonium diethyl phosphate, di(ethyltriphenylphosphonium) ethyl phosphate, tri(ethyltriphenylphosphonium) phosphate, methyltriphenylphosphonium dimethyl phosphate, methyltrioctylphosphonium dimethylphosphate, methyltriphenylphosphonium methyl methylphosphonate, and ethyltriphenylphosphonium diphenylphosphinate.

30 Another group of catalysts employed in the present invention are the phosphonium salts wherein the anion X is

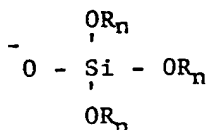
893191



wherein each R is as defined hereinbefore and wherein n has a
5 value of zero or 1.

Suitable such phosphonium salts include, for example, ethyltriphenylphosphonium ethyl sulfate, and di(ethyltriphenylphosphonium) sulfate.

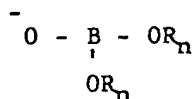
Another group of catalysts employed in the present in-
10 vention are the phosphonium salts wherein the anion X is



15 wherein each R is as defined hereinbefore and each n is 0 or 1.

Suitable such phosphonium salts include, for example, ethyltriphenylphosphonium triethyl silicate, di(ethyltriphenylphosphonium) diethyl silicate, tri(ethyltriphenylphosphonium) ethyl silicate, and tetra(ethyltriphenylphosphonium) silicate.

20 Another group of catalysts employed in the present in- vention are the phosphonium salts wherein the anion X is

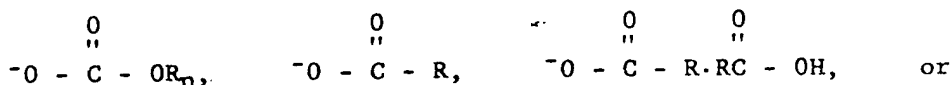


25 wherein each R is as defined hereinbefore and n is 0 or 1.

Suitable such phosphonium salts include, for example, ethyltriphenylphosphonium diethyl borate, methyltriphenylphosphonium dimethyl borate, di(ethyltriphenylphosphonium) ethyl
30 borate, tri(ethyltriphenylphosphonium) borate, and propyltriphenylphosphonium dipropyl borate.

893191

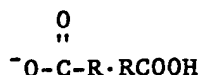
Another group of catalysts employed in the present invention are the phosphonium salts wherein the anion X' is



$^-\text{O} - \text{C} - \text{Z}_n - \text{C} - \text{OR}_n$ wherein each R is as defined hereinbefore, Z is a bivalent aliphatic hydrocarbon radical containing from 1 to 20 carbon atoms, and each n has a value equal to zero or 1.

Suitable such phosphonium salts include, for example, ethyltriphenylphosphonium acetate, di(ethyltriphenylphosphonium) carbonate, ethyltriphenylphosphonium ethyl carbonate, ethyltriphenylphosphonium ethyl oxalate, and di(ethyltriphenylphosphonium) oxalate.

In some instances, the phosphonium salts of a carboxylic acid employed as catalysts herein may contain some acid-salt complex without significantly adversely affecting the catalytic activity of the catalyst. In these instances, the anion X may be represented by the general formula



wherein R is as defined hereinbefore.

The phosphonium catalysts employed in the present invention are commercially available compounds and general procedures and references for their preparation are given in Organo Phosphorus Compounds, by G. M. Kosolapoff, John Wiley & Sons, 1958.

The internal phosphonium salts known as phosphobetaines may be prepared by the procedure outlined in the Journal of Organic Chemistry, Volume 27, pages 3403-3408, published in 1962.

Suitable such phosphobetaines include, for example, triphenyl-

propriophosphobetaine, and triphenylbutyrophosphobetaine.

The general reaction conditions employed in the process of the present invention for reacting the epoxide with the phenol in the presence of a catalyst are well known and include temperatures in the range of from 50° to 300°C under a pressure of from atmospheric to 150 psi (10.5 kg./cm.²) gauge.

The amount of the epoxide and the phenol to be employed in the process may vary over a wide range depending upon the type of reactants and the type of product to be desired.

Superior results of the new process are obtained when the higher molecular weight resins are prepared and in this case the ratios of reactants are varied depending upon the molecular weight desired and upon the type of end groups, i.e., whether the product is to be terminated with an epoxide or with a phenol. These high molecular weight resins are particularly useful as industrial coatings and primers.

The amount of the phosphonium catalyst employed in the process of this invention will vary over a wide range. In general, amount of catalyst will vary from 0.001% to 10% by weight, and preferably from 0.05% to 5% by weight of the reactants.

The reaction may be conducted in the presence or absence of solvents or diluents. In most cases, the reactants will be liquid and the reaction may be easily effected without the addition of solvents or diluents. However, in some cases, where either or both reactants are solids or viscous liquids it may be desirable to add diluents to assist in effecting the reaction. Examples of such materials include the inert liquids, e.g. ketones, inert hydrocarbons as xylene, toluene, and cyclohexane.

If solvents are employed in the reaction and the resulting product is to be used for coating purposes, the solvent may be retained in the reaction mixture. Otherwise, the solvent

893191

can be removed by any suitable method such as by distillation. Unlike inorganic bases or amines, it is not necessary to remove the phosphonium catalysts from the reaction mixture prior to curing of the resin produced thereby.

5 The products obtained according to the above process of reacting an epoxide with a phenol in the presence of the defined phosphonium catalysts are hydroxy ether compounds. Their physical characteristics will depend upon the reactants and proportions employed. In general, the products will vary from liquids
10 to solids, and in the case of the high molecular weight resins will vary from viscous liquids to hard solids. The products will possess at an aliphatic OH group formed by each reaction of an epoxide and a phenolic OH group, and can be further reacted through this group if desired. The polyfunctional reactants will
15 also give products terminated in phenolic OH groups and/or epoxy groups, and these will be available for further reaction.

A group of products which are particularly outstanding are those resins and polymers obtained by the reaction, in the presence of the catalysts herein defined, of the polyepoxides and
20 polyhydric phenols in controlled proportions. Those which use an excess of the polyepoxide will be terminated in epoxy groups and can be used as polyepoxides in known reactions. The high molecular weight polyepoxides are particularly useful in preparing surface coatings, adhesive, laminates, filament windings, coatings
25 for highways and airfields, structural applications, formation of foams and the like. Those prepared from the halogenated polyhydric phenols as shown hereinafter are particularly useful as flame proofing resins for forming laminates, coatings and the like.

Precatalyzed epoxy resin compositions are of particular
30 commercial interest. These precatalyzed systems are employed to prepare epoxy resins of higher molecular weight from low molecular

weight resins by transporting epoxy resin compositions containing a catalyst for promoting the reaction between a vicinal epoxide group and a hydroxyl-containing compound to other locations where such precatalyzed compositions are reacted with a compound
5 having about 2 hydroxyl groups to prepare epoxy resins of increased molecular weight. The catalysts employed in the process of this invention are particularly suited for this use.

The following examples are illustrative of the present invention.

10 EXAMPLE 1

To a reaction vessel equipped with a means for stirring, temperature indication and control and nitrogen purge was charged 326.1 grams of the diglycidyl ether of 4,4'-isopropylidenediphenol (bisphenol A) having an epoxide equivalent weight (EEW) of 187,
15 169.0 grams of 4,4'-isopropylidenediphenol (bisphenol A), 4.9 grams of the hydrolyzed product of the diglycidyl ether of 4,4'-isopropylidene diphenol, and 0.606 grams of ethyltriphenyl phosphonium diethyl phosphate dissolved in methanol. The reaction mass was heated at a rate of 5°C per minute. At a temperature of
20 about 130°C, an exotherm began and when the temperature reached 150°C, the heating was discontinued. The exotherm peaked at about 246°C. After the exotherm had subsided, the temperature was maintained at 180°C for 5 hours.

The resultant product was a frangible solid which had
25 a Gardner color of 1 and contained 2.71% epoxide.

EXAMPLE 2

The reaction of Example 1 was repeated, except that 0.703 grams of solid methyltriethylphosphonium dimethyl phosphate was employed as the catalyst.

30 The exotherm peak occurred at 240°C.

The product was a frangible solid which had a Gardner color of 1 and contained 2.00% epoxide.

EXAMPLE 3

The reaction of Example 1 was repeated except that 0.475 grams of ethyltriphenylphosphonium acetate, acetic acid complex dissolved in methanol was employed as the catalyst.

5 The peak exotherm occurred at about 240°C.

The product was a frangible solid which had a Gardner color of 1 and contained 2.35% epoxide.

EXAMPLE 4

10 The procedure of Example 1 was followed employing the following charge to the reaction vessel.

377.4 grams of the diglycidyl ether of bisphenol A having an EEW of 187,

5.7 grams of the hydrolysis product of the diglycidyl ether of bisphenol A,

116.9 grams of bisphenol A

15 0.694 gram ethyltriphenylphosphonium diethyl phosphate dissolved in methanol

The exotherm peak occurred at about 230°C, after which the resin was heated at 160°C for about 4 hours.

20 The product was a frangible solid which had a Gardner color of 1 and contained 8.24% epoxide.

EXAMPLE 5

Same procedure as in Example 4 except that the catalyst employed was 0.703 gram of ethyltriphenylphosphonium acetate, acetic acid complex dissolved in methanol.

25 The peak exotherm was about 230°C.

The product was a frangible solid which had a Gardner color of 1 and contained 8.15% epoxide.

EXAMPLE 6

30 Same procedure as in Example 4 except that 0.703 gram methyltriocetylphosphonium dimethyl phosphate, dissolved in methanol was employed as catalyst. The exotherm peak was about 230°C.

893191

The product was a frangible solid which had a Gardner color of 2 and contained 7.62% epoxide.

EXAMPLE 7

5 The procedure of Example 1 was followed employing the following charge to the reaction vessel.

346.3 grams of the diglycidyl ether of bisphenol A having an EEW of 187.

148.4 grams bisphenol A

5.3 grams of the hydrolysis product of the diglycidyl ether of bisphenol A

10 0.352 gram of ethyltriphenylphosphonium diethyl phosphate dissolved in methanol

The exotherm peak was about 245°C and the resin was heated at 170°C for about 4 hours.

15 The product was a frangible solid which had a Gardner color of 1 and contained 4.39% epoxide.

EXAMPLE 8

The procedure of Example 1 was followed employing the following charge to the reaction vessel.

20 320.2 grams of the diglycidyl ether of bisphenol A having an EEW of 187.

175.0 grams bisphenol A.

4.8 grams of the hydrolysis product of the diglycidyl ether of bisphenol A.

0.650 gram methyltrioctylphosphonium dimethyl phosphate.

25 The product was a frangible solid which had a Gardner color of 1 and contained 0.99% epoxide.

EXAMPLE 9

The reaction of Example 1 was repeated, except that the following charge was employed.

30 324.0 g. of the diglycidyl ether of bisphenol A having an EEW of 188,

893191

171.0 g. of bisphenol A

4.9 g. of the hydrolysis product of the diglycidyl ether of bisphenol A

0.48 g. ethyltriphenylphosphonium diphenylphosphinate dissolved in methanol

5 The peak exotherm was 225°C, after which the resin was heated at 180°C for 5 hours. The product was a frangible solid having an EEW of 2310.

EXAMPLE 10

10 The reaction of Example 1 was repeated, except that the following charge was employed.

324.0 g. of the diglycidyl ether of bisphenol A having an EEW of 188

171.0 g. of bisphenol A

4.9 g. of the hydrolysis product of the diglycidyl ether of bisphenol A

15 0.375 g. of methyltriphenylphosphonium methylmethylphosphonate dissolved in methanol

The exotherm peak was 211°C, after which the resin was heated at 180°C for 5 hours. The product was a frangible solid having an EEW of 2415.

20 EXAMPLE 11

The reaction of Example 1 was repeated, except that the following charge was used.

316.8 g. of the diglycidyl ether of bisphenol A, EEW = 188

178.4 g. of bisphenol A

25 4.8 g. of the hydrolysis product of the diglycidyl ether of bisphenol A

0.475 g. of triphenylpropiophosphobetaine

30 The peak exotherm was 245°C, after which the resin was heated at 180°C for five hours. The resultant product was a frangible solid having an EEW of 3160.

893191

Some of the foregoing examples employed small quantities of the hydrolyzed product of a liquid epoxide resin. This material is employed to improve the pigment dispersion characteristics of the resultant higher molecular weight resin being prepared. The presence of such hydrolyzed resins is not essential to the process of the present invention as is demonstrated in the following example.

EXAMPLE 12

A. To a reaction vessel equipped with a means for stirring, temperature control and indication, and nitrogen purge was charged 375.3 g. of the diglycidyl ether of bisphenol A having an epoxide equivalent weight (EEW) of 183, 124.7 g. of bisphenol A, and 0.456 g. of ethyltriphenylphosphonium diethyl phosphate dissolved in methanol. The reaction mass was heated at the rate of 5°C/minute. At a temperature of 130°C, an exotherm began and when the temperature reached 150°C, the heating was discontinued. The exotherm peak was 228°C. After the exotherm subsided, the temperature was maintained at 160°C for 4 hours. The resultant product was a frangible solid having an EEW of 548.

B. The method of the above example was repeated except that the following charge was employed.

371.8 g. of the diglycidyl ether of bisphenol A (EEW = 183)

5.6 g. hydrolysis product of the diglycidyl ether of bisphenol A

122.6 g. of bisphenol A

0.456 g. ethyltriphenylphosphonium diethyl phosphate dissolved in methanol

After an exotherm peak of 226°C, the resin was heated at 160°C for 4 hours. The product was a frangible solid having an EEW of 547.

EXAMPLE 13

To a reaction vessel equipped with a means for stirring, temperature indication and control, water jacketed condenser and nitrogen purge was charged 322.0 g. of the diglycidyl ether of bisphenol A having an epoxide equivalent weight (EEW) of 183, 178.0 g. of 2,6,2',6'-tetrabromo-4,4'-isopropylidinediphenol (tetrabromobisphenol A), and 0.77 g. of a 25% methanol solution of ethyltriphenylphosphonium diethyl phosphate (0.192 g. of actual catalyst.). The reaction mass was heated at a rate of 5°C/minute to 150°C. After two hours, the temperature was reduced to 100°C, 125 grams acetone was added slowly through the condenser, and the mixture was stirred until a uniform solution was obtained. The resultant product was a viscous liquid having an EEW of 470 and a viscosity of 925 centipoise at 25°C.

15 EXAMPLE 14

The procedure of Example 13 above was followed employing the following charge to the reaction vessel.

256 g. of diglycidyl ether of bisphenol A (EEW = 183)
 64 g. of glycidyl ether of a novolac resin, (EEW = 178), i.e. and a functionality of 3.5, phenol-formaldehyde condensate.
 180.0 g. 2,6,2',6'-tetrabromo-4,4'-isopropylidinediphenol.
 0.64 g. of a 25% methanol solution of ethyltriphenylphosphonium diethyl phosphate (0.16 g. of actual catalyst)

25 After 2 hours at 150°C, the mixture was cooled to 100°C, and 125g. acetone was added slowly through the condenser with thorough agitation until homogeneity was achieved. The resultant product was a viscous liquid having an EEW of 463 and a viscosity of 1160 centipoise at 25°C.

30 EXAMPLE 15

The process of the present invention is particularly

useful in the preparation of higher molecular weight solid epoxy resins from lower molecular weight liquid epoxy resins by the pre-catalyzed method. In this method, the liquid epoxide resin is blended with the catalyst and oftentimes it is stored in warehouses where high temperatures are encountered for prolonged periods of time before being reacted with the diphenolic compound. The following two experiments demonstrate that a less colored product is obtained when the catalysts of the present invention are employed as compared to the phosphonium catalysts of the prior art.

A. A mixture containing 326.0 grams of the diglycidyl ether of bisphenol A having an EEW of 188, 4.8 grams of the hydrolysis product of the diglycidyl ether of bisphenol A, and 0.398 grams ethyltriphenylphosphonium diethyl phosphate was heat aged in an oven at 80°C for 7 days, after which time the resin was reacted with 169.0 grams of bisphenol A employing the procedure of Example 1. The peak exotherm was 242°C. The resultant product had an EEW of 2070 and a Gardner color of 1.

B. Comparative experiment

A mixture containing 319.0 grams of the diglycidyl ether of bisphenol A having an EEW of 191, 4.8 grams of the hydrolysis product of the diglycidyl ether of bisphenol A and 0.972 grams of ethyltriphenylphosphonium iodide was heat aged in an oven at 80°C for 6 days, after which time the resin was reacted with 163.9 grams of bisphenol A employing the procedure of Example 1. The peak exotherm was about 235°C. The resultant product had an EEW of 2100 and a Gardner color of 4.

The above example clearly demonstrates the improved color of polyepoxides prepared from precatalyzed epoxy resin systems containing the catalysts of the present invention over those of the prior art.

893191

EXAMPLE 16

The following example demonstrates the undesirable color formation when employing amine catalysts.

A. Comparative Example

5 Employing the procedure of Example 1, 374.9 grams of the diglycidyl ether of bisphenol A having an EEW of 189 was reacted with 119.5 grams of bisphenol A in the presence of 0.684 gram of benzyltrimethylammonium chloride (7.6 grams of a 10% methanol solution). After the exotherm, the reaction was main-
10 tained at 160°C for 4 hours. The product was a frangible solid which had a softening point of about 77°C, a Gardner color of 4 and a % epoxide of 7.85.

B. Comparative Example

15 The reactants and procedures of A above was conducted in the presence of 0.375 grams of N-methylmorpholine as catalyst. The product was a frangible solid which had a melting point of about 78.5°C, a Gardner color of 3 and a % epoxide of 7.78%.

EXAMPLE 17

20 The following experiments demonstrate that higher molecular weight resins can be prepared when a catalyst of the present invention is employed as compared to a phosphonium halide catalyst.

25 A. A high molecular weight thermoplastic polymer was prepared according to the process of this invention by charging 239.7 grams of a diglycidyl ether of bisphenol A having an epoxide equivalent weight of 170.6 and 160.3 grams of recrystallized bisphenol A to a reaction vessel equipped as in Example 1. To this mixture, 71.0 grams of the monoethylether of ethylene-
30 glycol was added as a diluent in order to facilitate stirring. After adding 0.959 grams of the acetic acid complex of ethyltriphenylphosphonium acetate dissolved in methanol, the reaction

893191

mixture was heated to 150°C at a rate of 5°C per minute. The reaction mass exothermed to a peak of 184°C. After the exotherm had subsided, the temperature was maintained at 140-150°C for about 2 hours. The heating was discontinued, and methylethyl ketone was added to the reaction mass until the non-volatiles content was 40% to facilitate handling. The resultant resin had a % epoxide of 0.15% and a peak molecular weight of the most abundant species of 16,000 as determined by gel permeation chromatography.

10

B. Comparative Example

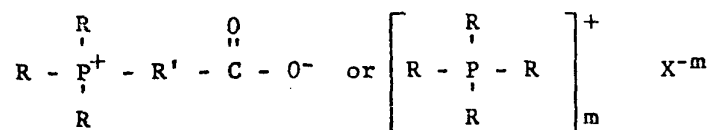
The procedure and charge of Example A above was employed except that the catalyst employed was 1.148 grams of ethyltriphenylphosphonium iodide. The exotherm peak was 173°C and the resin was heated for 4 hours before diluting to 40% non-volatiles with methylethyl ketone. The resultant resinous product had an epoxide content of 0.35% and a peak molecular weight of the most abundant species of 9,000.

20

893191

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for preparing a hydroxy ether by reacting an aromatic hydroxy-containing compound with a 1,2-epoxy-containing compound in presence of a catalyst characterized in that the catalyst employed is a phosphonium salt having the
5 formula



10 wherein each R is hydrogen, an aliphatic hydrocarbon radical containing from 1 to 20 carbon atoms, an aromatic hydrocarbon radical, an alkyl substituted aromatic hydrocarbon radical, or -R''Y wherein R'' is an aliphatic hydrocarbon radical having from 1 to 20 carbon atoms and Y is Cl, Br, I, NO₂, or OH; R' is an
15 alkylene group having from 2 to 20 carbon atoms; X is the anion portion of an acid or acid ester selected from carboxylic, polycarboxylic, carbonic, phosphoric, phosphonic, phosphinic, nitric, nitrous, sulfuric, sulfinic, sulfonic, silicic, and boric acids; and m is the valence of the anion X.

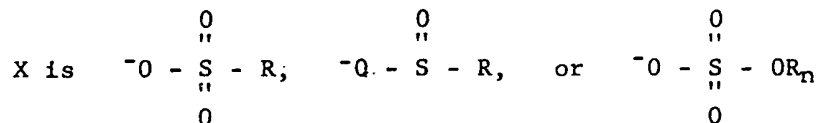
2. A process as defined in Claim 1 wherein the anion
X is $\overset{\text{O}}{\parallel} \text{O} - \text{N} = \text{O}$ or $\overset{\text{O}}{\parallel} \text{O} - \text{N} = \text{O}$.

3. A process as defined in Claim 1 wherein the anion
X is $\overset{\text{O}}{\parallel} \text{O} - \text{P} - \text{OR}_n$, $\overset{\text{O}}{\parallel} \text{O} - \text{P} - \text{OR}_n$, or $\overset{\text{O}}{\parallel} \text{O} - \text{P} - \text{R}$
0 - R_n R R

5 wherein each R is as defined in Claim 1 and each n is 0 or 1.

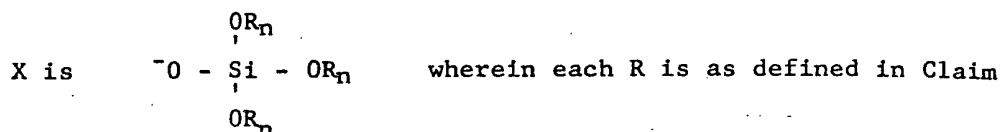
893191

4. A process as defined in Claim 1 wherein the anion



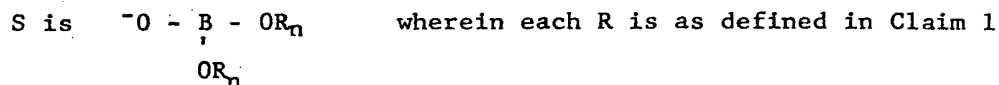
5 wherein R is as defined in Claim 1 and n is 0 or 1.

5. A process as defined in Claim 1 wherein the anion



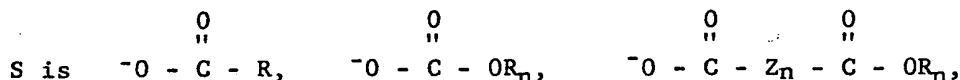
5 1 and each n is 0 or 1.

6. A process as defined in Claim 1 wherein the anion



and each n is 0 or 1.

7. A process as defined in Claim 1 wherein the anion



5 or $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ ^-\text{O} - \text{C} - \text{R} \cdot \text{R} - \text{C} - \text{OH} \end{array}$ wherein each R is as defined in Claim 1, Z is a bivalent aliphatic hydrocarbon radical containing from 1 to 20 carbon atoms or a bivalent aromatic hydrocarbon radical, and each n is 0 or 1.

8. A process as defined in Claim 1 wherein each R is

alkyl having from 1 to 8 carbon atoms or phenyl, R' is ethylene, and X is the anion portion of dimethyl or diethyl phosphate, dimethyl- or diphenyl-phosphinic acid, or acetic acid.

9. A process as defined in Claim 1 wherein the

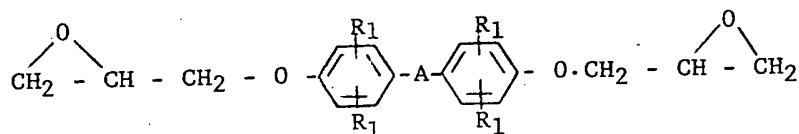
catalyst is ethyltriphenylphosphonium diethyl phosphate, methyl-

893191

trioctylphosphonium dimethyl phosphate, ethyltriphenylphosphonium
acetate-acetic acid complex, ethyltriphenylphosphonium diphenyl-
5 phosphinate, methyltriphenylphosphonium methyl methylphosphonate,
or triphenylpropiophosphobetaine.

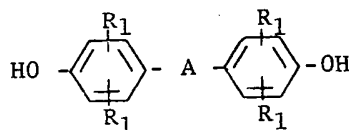
10 A process as defined in Claim 1 wherein the 1,2-
epoxy-containing compound is a polyepoxide.

11. A process as defined in Claim 10 wherein the poly-
epoxide has the general formula



wherein each R_1 is hydrogen, bromine, or chlorine, and A is an
alkylene or alkylidene group having from 1 to 4 carbon atoms,
-S-, -S-S-, -SO-, -SO₂-, -CO-, or -O-.

12. A process as defined in Claim 1 wherein the
aromatic hydroxy-containing compound is a bisphenol having the
formula



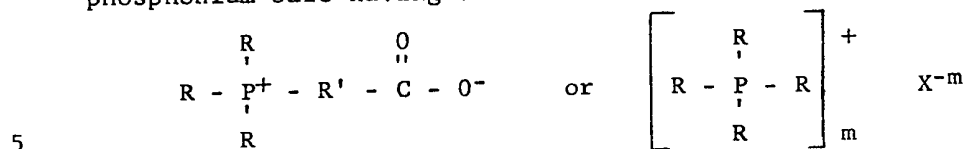
wherein each R_1 is hydrogen, bromine, or chlorine, and A is an
alkylene or alkylidene group having from 1 to 4 carbon atoms,
-S-, -S-S-, -SO-, -SO₂-, -CO-, or -O-.

13. A process as defined in Claim 1 wherein the
reaction is carried out at a temperature within the range of
from 50 to 300°C. under a pressure of from atmospheric to 150
psi (10.5 kg./cm.²) gauge.

893191

14. A process as defined in Claim 1 wherein the catalyst is employed in an amount of from 0.001 to 10 weight per cent based on the weight of the reactants.

15. A composition comprising a polyepoxide and a phosphonium salt having the formula



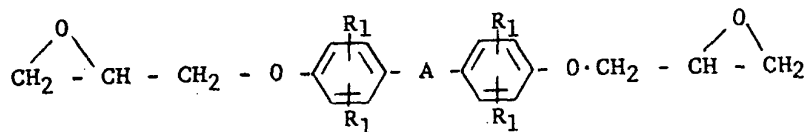
10 wherein each R is hydrogen, an aliphatic hydrocarbon radical containing from 1 to 20 carbon atoms, an aromatic hydrocarbon radical, an alkyl substituted aromatic hydrocarbon radical, or -R''Y wherein R'' is an aliphatic hydrocarbon radical having from 1 to 20 carbon atoms and Y is Cl, Br, I, NO₂, or OH; R' is an alkylene group having from 2 to 20 carbon atoms; X is the anion portion of an acid or acid ester selected from carboxylic, polycarboxylic, carbonic, phosphoric, phosphonic, phosphinic, nitric, nitrous, sulfuric, sulfinic, sulfonic, silicic, and boric acids; 15 and m is the valence of the anion X.

16. A composition as defined in Claim 15 wherein each R is alkyl having from 1 to 8 carbon atoms or phenyl, R' is ethylene, and X is the anion portion of dimethyl or diethyl phosphate, dimethyl- or diphenyl-phosphinic acid, or acetic acid.

17. A composition as defined in Claim 15 wherein the phosphonium salt is ethyltriphenylphosphonium diethyl phosphate, methyltrioctylphosphonium dimethyl phosphate, ethyltriphenylphosphonium acetate-acetic acid complex, ethyltriphenylphosphonium 5 diphenylphosphinate, methyltriphenylphosphonium methyl methylphosphonate, or triphenylpropiophosphobetaine.

893191

18. A composition as defined in Claim 15 wherein the polyepoxide has the general formula



5

wherein each R_1 is hydrogen, bromine, or chlorine, and A is an alkylene or alkylidene group having from 1 to 4 carbon atoms, -S-, -S-S-, -SO-, -SO₂-, -CO-, or -O-.

